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Dated

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9190

2. Patent application number

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9912842.3

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BP EXPLORATION OPERATING COMPANY LIMITED
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EC2M 7BA

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

ENGLAND, UNITED KINGDOM

6225916002

4. Title of the invention

PROCESS FOR REDUCING THE ACIDITY OF OIL

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

SMITH, Julian Philip Howard
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7058935001

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Country

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Number of earlier application

Date of filing
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- a) any applicant named in part 3 is not an inventor, or
 - b) there is an inventor who is not named as an applicant, or
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Continuation sheets of this form

Description 8

Claim(s) -

Abstract -

Drawing(s) 2

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Priority documents

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Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

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11. I/We request the grant of a patent on the basis of this application.

Signature
SMITH, Julian Philip Howard

Date 02.06.1999

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Process for reducing the acidity of oil

This invention relates to a process for the de-acidifying of crude oil and/or a crude oil distillate.

Crude oil and distilled fractions thereof may contain acid impurities such as naphthenic acid. Typical TAN values for such acidic oils are in the range of 0.5 to 4 mg
5 KOH/g. These acid impurities can cause corrosion problems, particularly in refinery operations where temperatures of 200°C and above are encountered. For this reason, it is desirable to reduce the acidity of crude oils, for example, by reducing the amount of naphthenic acid present.

Various methods for deacidifying crude oil and/or crude oil distillate (hereinafter
10 "oil") are known. In a conventional de-acidification process, an alkali such as aqueous sodium hydroxide is contacted with the oil to neutralise any acid present. The reaction produces an aqueous phase comprising water, and alkali naphthenate. This aqueous phase has to be removed from the deacidified oil, before the oil can be used or sold.

According to US 4 199 440, sodium naphthenate is chemically similar to soap,
15 and tends to emulsify hydrocarbon and aqueous phases. This emulsion interferes with the efficient separation of the deacidified oil and aqueous phase. This problem may be alleviated by using a dilute solution of the aqueous base because the solubility of alkali naphthenates in the aqueous phase increases as the concentration of alkali in the aqueous phase decreases. Thus by using a dilute solution of sodium or potassium hydroxide, the
20 tendency of alkali naphthenate to emulsify hydrocarbon phases is reduced.

EP 0 881 274 endeavours to improve the process of US 4 199 440 by avoiding the formation of a stable emulsion. This is achieved by adding the acidic crude oil with

only mild agitation to the aqueous base in a sufficient ratio to produce a dispersion of oil in a continuous aqueous base phase. Large volumes of aqueous base are required as stable emulsions are said to form if the ratio of oil to aqueous base is 1:1 or less.

Typically, oil to base ratios are of 1:3 to 1:15, preferably 1:3 to 1:4 (based on the weight of oil and water) are employed.

The large volume of aqueous base required in EP 0 881 274 makes the process relatively uneconomic, particularly when very large volumes of oil require treatment. Thus, it is desirable to reduce the amount of aqueous base required to deacidify a given quantity of oil.

WO 97/08270 describes a process in which a base is contacted with oil, in the presence of water in an amount of from 0 to 7 wt % of oil. To avoid problems associated with stable emulsion formation, however, the deacidification process is carried out under conditions, such that following neutralisation, any water present in the reaction mixture is removed. Thus, any solid suspended in the oil after treatment is dispersed throughout the oil, and must be separated by centrifugation. Whilst this process may be effective for treating oil on a small-scale, it cannot be used to treat large quantities of oil in an efficient manner. This is because the rate of deacidification is limited by the constraints of having to centrifuge the entire volume of oil treated.

We have now found that with certain bases, a demulsifier can be employed to ensure that even in the presence of relatively low concentrations of water, oil can be treated with base to produce at least three separate phases: an oil-rich phase consisting essentially of deacidified oil, an aqueous phase consisting essentially of water, and an interface layer disposed between the oil-rich phase and aqueous phase. The interface layer comprises accumulated solids, such as neutralisation salts. The interface layer is immiscible with both the deacidified oil and water, and is thus easily removed.

According to the present invention, there is provided a process for de-acidifying crude oil and/or crude oil distillate, said process comprising:

- a) contacting crude oil and/or crude oil distillate with a Group IIA metal hydroxide in the presence of water, wherein water is present in a concentration of 0.01 to 100 wt % of the crude oil and/or crude oil distillate; and
- b) introducing a demulsifier to the mixture of crude oil and/or crude oil distillate, Group IIA metal hydroxide and water, in an amount effective to cause the

mixture to separate into an oil-rich phase, an aqueous phase and an interface layer disposed between the oil-rich phase and aqueous phase.

Steps a) and b) of the present invention may be carried out at 5 to 200°C, preferably 10 to 70°C, most preferably, 20 to 50°C, and especially 30 to 40°C.

- 5 Preferably also, the process is carried out without heating the oil using an external or dedicated heat source.

In step a), crude oil and/or crude oil distillate (hereinafter "oil") is contacted with Group IIA metal hydroxide in the presence of water, to produce water and neutralisation salts. This neutralisation reaction causes the acidity of the oil to be reduced, such that, 10 preferably, the treated oil may be used directly, exported, sold or further processed, for example, by fractional distillation.

Suitable Group IIA metal hydroxides include barium hydroxide, magnesium hydroxide, and preferably, calcium hydroxide. Group IIA metal hydroxides tend to be relatively insoluble in water (and oil), such that any excess hydroxide remains 15 substantially undissolved in the aqueous phase (and oil-rich phase). Thus, the aqueous phase consists essentially of water and is either neutral, or only very mildly alkaline. Moreover, the neutralisation salts produced when Group IIA metal hydroxide is reacted with, for example, naphthenic acid, tend to be substantially insoluble in water and oil (eg calcium naphthenate). Such salts do not emulsify the oil and aqueous phases, and 20 instead, are easily recoverable from the remainder of the reaction mixture, as the demulsifier causes them to accumulate together with any unreacted solid base at the interface layer, between the oil-rich and aqueous phases.

Step a) is carried out in the presence of water in a concentration of 0.01 to 100 wt % of oil. Water is believed to aid the neutralisation reaction by catalysing the transfer 25 of hydrogen ions between the oil and base. Water is also required for the formation of the aqueous phase and interface layer. Preferably, water concentrations of 0.01 to 30, more preferably 0.01 to 25 wt %, even more preferably, 0.1 to 20 wt %, most preferably, 3 to 20 wt %, and especially 10 to 15 wt % are employed. To achieve these concentrations, water may be added to the reaction mixture. Water is also produced 30 during the deacidification reaction.

A surfactant may also be added to the reaction mixture. This surfactant may catalyse the neutralisation reaction further by aiding the transfer of hydrogen ions

between the oil and base. Examples of suitable surfactants include Atloz[™] LP6, TBAB, Hyperman[™] B246 and CTAB. Surfactant concentrations of 0.01 to 40 wt %, preferably 5 to 20 wt % and most preferably, 5 to 15 wt % of the calcium hydroxide employed are suitable.

5 In an embodiment of the present invention, the base is formed into a slurry before being contacted with the oil. Preferably, the slurry comprises water and, optionally, a surfactant and/or organic solvent. Suitable organic solvents include decane, crude oil, DDW, kerosene, DCP202 and mixtures thereof.

10 Once the base is contacted with the oil, the resulting mixture may be stirred or agitated in a mixing unit. The mixture may be stirred using a mechanical stirrer, an ultrasonic stirrer or by bubbling an inert gas through the reaction mixture. The mixing step may last 2 to 30 minutes, preferably, 5 to 20 minutes and most preferably, 8 to 15 minutes. The mixing step may be carried out at 5 to 200°C, preferably 10 to 70°C, most preferably, 20 to 50°C, and especially 30 to 40°C.

15 In step b), a demulsifier is added to the reaction mixture. After the addition of a demulsifier, the reaction mixture may be allowed to settle, for example, in a settling unit. This causes the reaction mixture to separate into at least three phases: an oil-rich phase, aqueous phase and an inter-face layer disposed between the aqueous and oil-rich phases. The oil-rich phase may be isolated from the settling unit and used directly, sold or further
20 processed, for example, by fractional distillation.

 The demulsifier ensures that the water present in the reaction mixture separates from the oil phase. Water is present in the aqueous phase, and is usually also be present in the interface layer. The demulsifier also ensures that any solids present in the reaction mixture (eg unreacted base and/or salt of neutralisation) gather as a layer at the interface
25 of the oil-rich and aqueous phases. This interface layer may be regarded as consisting essentially of an aqueous suspension of the solid product of the neutralisation reaction and any unreacted solid base (eg calcium hydroxide). This layer usually also contains some deacidified oil. In one embodiment, this deacidified oil is recovered from the remainder of the aqueous phase by using a hydrocyclone, electrostatic coalescer and/or,
30 preferably, a centrifuge. The recovered deacidified oil may be used directly, exported or processed.

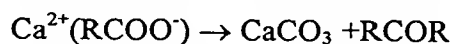
 The water in the aqueous phase and/or inter face layer may have formed during

the course of, for example, steps a) and/or b). Alternatively or additionally, the water may have been added some time during the deacidification process. Suitable demulsifiers include ML 3407. The concentration of demulsifier employed may be 0.01 to 5 wt %, preferably, 0.1 to 2 wt % and especially 0.1 to 0.5 wt % of oil.

5 The inter face layer may represent 1 to 40 vol %, preferably, 5 to 20 vol %, and especially 8 to 11 vol % of the total volume of the reaction mixture. Thus, the volume of fluid required to be processed in, for example, a hydrocyclone, electrostatic coalescer and/or centrifuge is relatively small compared to the total volume of the reaction mixture.

10 Optionally, some of the water in the inter face layer phase may be separated prior to treatment of the layer by allowing the isolated aqueous phase to settle in a further separation step. This water, which is substantially free of suspended solid, may be removed, and optionally recycled for re-use.

15 Solids recovered from the inter face layer include unreacted base and neutralisation salts. These solids may be converted into useful feedstocks. For example, some calcium salts of organic acids, can be pyrolysed to produce ketones and calcium carbonates according to the following equation:



20 Thus, in a preferred embodiment of the present invention, solids recovered from the inter face layer are heated to a temperature of 700 to 900°C, preferably, 750 to 850°C. The process is particularly suitable for producing naphthenic ketones, for example, from calcium naphthenates.

The process of the present invention may be employed to reduce TAN values of oils to 0 to 2 mg KOH/g, preferably, 0.1 to 0.8 mg KOH/g and especially, 0.1 to 0.5 mg KOH/g.

25 The process of the present invention may be carried out on a refinery, or whilst the oil is being transported, for example, in a tanker at sea.

Embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings in which:

30 Figure 1 is a schematic diagram of an apparatus for carrying an embodiment of the process of the present invention, and

Figure 2 shows the area labelled "A" in Figure 1 in greater detail.

Referring to Figures 1 and 2, the apparatus 10 comprises a slurry mixing tank 12,

a static mixer 14, a series of reaction tanks 16, a coalescer 18 and a centrifuge 20. The slurry mixing tank 12 is coupled to a supply 22 of calcium hydroxide. The mixing unit 14 is fed with acid crude oil 24.

5 In use, calcium hydroxide, water and a surfactant are introduced into the slurry mixing tank 12, where they are mixed into a slurry comprising 5 - 10 % calcium hydroxide by weight of slurry. The slurry further comprises a CTAB surfactant.

The neutralisation reaction is initiated when the slurry is contacted with the acidified oil. This occurs when the slurry is added to the acid crude 24 via an injection quill 26. The resulting reaction mixture passes through a static mixer 14, where the
10 mixture is dispersed, and then into the reaction tanks 16, where it has a residence time of between 5 and 20 minutes, where the neutralisation reaction takes place.

During neutralisation, calcium hydroxide acts as a base, and reacts with any acid present in the oil to produce a neutralisation salt and water. Examples of neutralisation salts include calcium naphthenate. Like calcium hydroxide, this compound is
15 substantially insoluble in water and oil. The neutralisation reaction is catalysed by the presence of water.

The reaction mixture emerging from the reaction tanks 16, is fed into the coalescer 18. The coalescer 18 comprises a cyclonic coalescer 18a, and a separator coalescer 18b. The cyclonic coalescer promotes the agglomeration of the solid particles
20 prior to entering the separator coalescer 18b. Once the mixture is transferred into the separator coalescer 18b, the reaction mixture is allowed to separate, in the presence of a demulsifier, into an oil-rich phase 28, an aqueous phase 30 and an interface or "ragging" layer 32. The demulsifier may be added to the mixture at point X, Y or both (see Figure 1). The interface layer 32 is disposed between the oil-rich phase 28 and the aqueous
25 phase 30 (see Figure 2).

The oil-rich phase 28 consists essentially of deacidified oil. This phase 28 is the least dense of the three phases, and is withdrawn from the separator coalescer 18b via line 34. Once withdrawn, the oil-rich phase 28 is ready for use, export, or further processing, for example, by fractional distillation.

30 The aqueous phase 30 consists essentially of water, and is transferred from the separator coalescer 18b into a water break tank 36, prior to being recycled to the slurry mixing tank 12. Fresh water 40 may be added to the tank 36, if required.

The interface layer 32 is an aqueous suspension comprising calcium naphthenate and water and some deacidified oil. Other insoluble solids such as unreacted calcium hydroxide may also be present in this phase. This interface layer is introduced into the centrifuge 20, where it is separated into three streams, each consisting essentially of water 42, deacidified oil 44 and solids 46. The water is recycled back to the slurry mixing tanks 12 via the water break tank 36, and the oil is returned to the main oil stream from the outlet of the separator coalescer. The solids 46 comprise calcium naphthenate and unreacted calcium hydroxide, and can be processed into useful chemical feedstocks, for example, by pyrolysis.

10 **Example**

In this Example, the rate of deacidification achieved when acidic crude oil was contacted with a slurried mixture of calcium hydroxide, surfactant and water, was compared to the rate achieved when the oil was contacted with a non-slurried mixture of calcium hydroxide, surfactant and water.

15 Calcium hydroxide (0.10g), surfactant (CTAB, 10 wt % $\text{Ca}(\text{OH})_2$), and water (5g) were mixed into a slurry in a preliminary step. 100g of acidified oil (FPS/Hard, TAN = 1.14 mg KOH/g) and 5g decane were then contacted with the slurry at a temperature of 40°C. The resulting mixture was stirred for 10 minutes and a demulsifier (ML3407, 2 drops) was added. The mixture was then allowed to settle. After 5
20 minutes, the mixture separated into three phases: an oil-rich phase, an aqueous phase, and an interface layer. The TAN of the oil was measured 20, 30 and 40 minutes after the addition of the demulsifier, and recorded as shown in the Table below.

The above procedure was repeated except that the preliminary slurring step was omitted. Instead, the oil and decane were contacted directly with a non-slurried mixture
25 of calcium hydroxide, water and surfactant.

Table

Sample	Surfactant additive	Water (%)	Mixing time (minutes)	TAN BP 408 Acidity mg KOH/g		
				Elapsed Time (minutes)		
				20	30	40
no slurry	CTAB	5	10*	0.21	0.20	0.19
slurry	CTAB	5	10*	0.13	0.15	0.11

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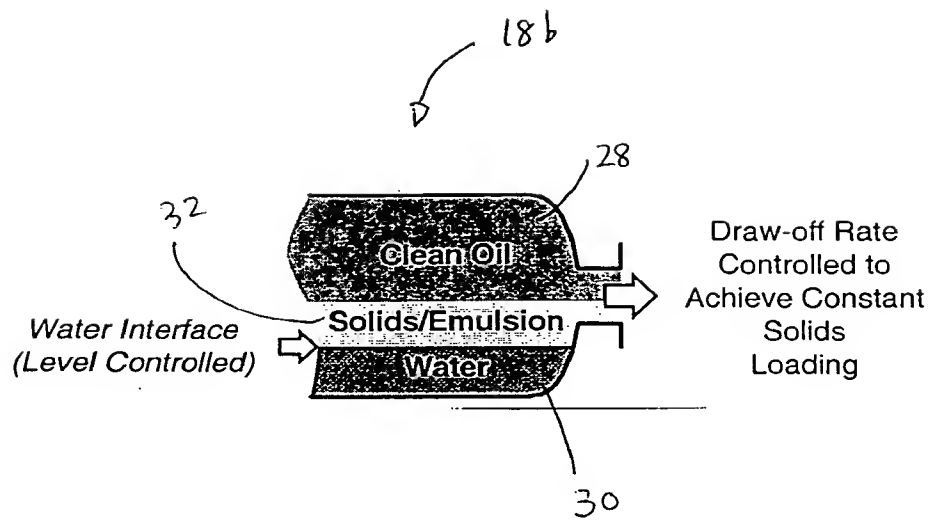


FIGURE 2

